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WO 98/13456 A1

WO 98-13456

Translated from German by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

Code: 1505-72663

INTERNATIONAL PATENT OFFICE
WORLD ORGANIZATION FOR INTELLECTUAL PROPERTY
International patent published on
the basis of the Patent Cooperation Treaty (PCT).
INTERNATIONAL PUBLICATION NO. WO 98/13456 A1

International Patent Classification ⁶ :	C 11 D 3/22 1/62
International Application No.:	PCT/EP97/05092
International Application Date:	September 17, 1997
International Publication Date:	April 2, 1998
Priority	
Date:	September 26, 1996
Country:	DE
No.:	196 39 602.9

WASHING OR LAUNDERING POST-TREATMENT AGENTS

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Designated States:

PL, European Patent (AT, BE, CH,
DE, DK, ES, FI, FR, GB, GR, IE, IT,
LU, MC, NL, PT, SE).

Published

With international search report.

Will be republished if changes to the claims are submitted before the end of the period permitted for such changes.

Abstract

The invention relates to powder, pasty or liquid washing or laundering post-treatment agents containing cyclodextrin, cyclodextrin derivatives as additives and substances forming cyclodextrin or cyclodextrin derivatives or their mixtures in the rinsing liquid. The tenside residues on textile surfaces can be efficiently reduced by using said substances.

This invention concerns a powder, paste or liquid washing or laundering post-treatment, which contains cyclodextrin, and a method for treatment of textiles.

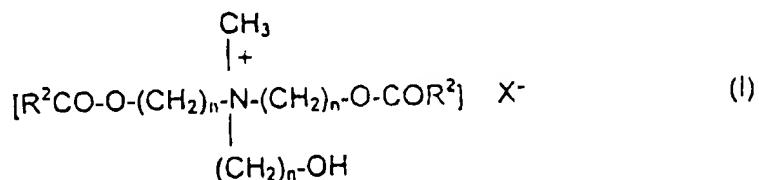
In a washing process for washing textiles, after the wash cycle in which a conventional detergent is used, the textiles are rinsed with water in one or more rinse operations in order to remove the detergents. Here the individual detergent components are not all rinsed out to the same extent. Particular problems are presented by the nonionic surfactants, which are deposited on the textile fibers. Another problem in connection with residues of this kind lies in the formation of foam during the rinsing operations, which are particularly unpleasant in the home laundry and can lead to operating problems in a commercial laundry, especially in continuously operating washing lines.

In commercial laundries acidifying agents and/or fabric softeners or softening agents are, as a rule, added to the rinse water in at least one rinsing operation, preferably in the last rinsing operation. Fabric softeners or softening agents are also customary in the rinse cycle in household washing machines.

Acidification agents usually contain acids like phosphoric acid, acetic acid, hydrochloric acid, glycolic acid, citric acid, lactic acid or formic acid and are intended to reduce the relatively high pH produced by the alkaline detergents.

Fabric softeners or softening agents are supposed to improve the feel and appearance of textiles and to give them antistatic properties. Agents of this kind usually contain cationic surfactants, for example, quaternary ammonium compounds. These compounds are deposited on the surface of the textiles, so that the charge on the surface of the textiles is changed and the desired properties are obtained.

Conventional textile softeners or softening agents are, for example, compounds of the type of the so-called ester quats. These compounds are industrially quaternized di-fatty acid-trialkanolamine ester salts, which are usually obtained by the reaction of trialkanolamines like triethanolamine or tripropanolamine with fatty acids or fatty acid esters and subsequent reaction of the di-fatty acid esters that have formed with methyl chloride or dimethyl sulfate. They correspond to formula I



in which R^2CO stands for an aliphatic acyl residue with 12 to 22 carbon atoms and 0, 1, 2 or 3 double bonds, n stands for 2 or 3 and X stands for halide, methosulfate or methophosphate.

These compounds are widely used as softening agents. Thus, liquid detergents are described in International Patent Application No. WO 94/06899, which contain as fabric softeners quaternary ammonium compounds of formula I, alkyl glycosides and other surfactants. These agents can contain from 10 to 50 wt%, with respect to the detergent, of a mixture of quaternary compounds of formula I and alkyl glycosides. The said quaternary ammonium compounds by their nature tend to hydrolyze at the acyl residue in an aqueous medium. According to European Patent Application No. EP-A-239,910 cationic softeners of the type of ester quats that are in a 0.5 to 1.5% solution show optimum hydrolysis stability in an aqueous medium at a pH value between 2.5 and 4.2. Above and below this range the aqueous active agent dispersions become increasingly unstable due to hydrolytic decomposition.

One strives to keep the amount of detergent residues on the textiles as low as possible. Surfactants like anionic and nonionic surfactants can be found on textile surfaces as residues of this kind. However, especially the nonionic surfactants tend to form significant amounts of foam even in very small amounts. For this reason one strives to minimize the residual content of nonionic surfactants and, as far as possible, not to exceed residual content of 200 ppm with respect to the amount of laundry.

This invention was based on the task of making available a washing or laundry post-treatment agent that makes a clear reduction of the residual surfactant content on textiles, in particular the content of nonionic surfactants, where a limiting value of 200 ppm with respect to the amount of laundry is not supposed to be exceeded.

Accordingly, an object of the invention is a powder, paste or liquid laundry or detergent post-treatment agent, which is characterized by the fact that it contains as additive cyclodextrin, cyclodextrin derivatives or substances that form cyclodextrin or cyclodextrin derivatives in the wash water or mixtures of these.

Surprisingly it was found that through the use of the agent in accordance with the invention the content of surfactant residues, especially nonionic surfactants, on textiles can be clearly reduced.

The use of cyclodextrins in the field of detergents and cleaning agents is already known from the prior art. A cleaning agent that contains at least one cyclodextrin or cyclodextrin derivative as active cleaning component is described in International Patent Application No. WO 94/10280. The described agent is used in particular to remove oils, fats, aliphatic and aromatic hydrocarbons, acids, esters and ethers from surfaces of any kind.

A method for producing solid particles of water-sensitive materials, where particulate complexes of cyclodextrins and fragrances are provided with a protective coating, is described in International Patent Application No. WO 93/05136.

Cyclodextrins, also called cycloglucans, are formed in the degradation of starch by *Bacillus macerans* or *B. circulans* under the effect of cyclodextrin glycosyl transferase. The cyclodextrins as a rule consist of 6, 7 or 8 α -1,4-linked glucose units. The use of cyclodextrins or their derivatives as active cleaning components is described, for example, in International Patent Application No. WO 94/10280. Surprisingly, it was now established that when cyclodextrins or their derivatives or substances that form these compounds *in situ* in the rinse liquid are added, the deposition of nonionic surfactants on the textile surface can be inhibited.

The agent in accordance with the invention can contain any cyclodextrin monomers, for example, α -, β - or γ -cyclodextrins. Likewise suitable are all cyclodextrin derivatives such as, for example, cyclodextrin carbonates, ethers or polyethers, or cyclodextrin derivatives in which one or more of the hydroxy groups are substituted by functional residues. Such functional residues include, for example, C₁₋₄ alkyl, especially methyl or ethyl, hydroxyethyl, hydroxypropyl or acetyl groups. Especially suitable are residues through which the water solubility of the cyclodextrin is increased. Also, any mixtures of cyclodextrin and more and/or [sic] cyclodextrin derivatives can be used.

As substances that form cyclodextrin or cyclodextrin derivatives *in situ* in the rinse liquid one may mention those substances that form cyclodextrins in the presence of cyclodextrin glycosyl transferase. A combination of cyclodextrin glycosyl transferase and amylase has proven to be particularly advantageous, since amylase is a cheap and ecologically harmless substance.

The cyclodextrins can be contained in the agents in accordance with the invention in an amount of 0.5 wt% to 10 wt%, in particular 0.5 to 5 wt%, with respect to the agent. The agents in accordance with the invention are dispensed into the wash or rinse liquid preferably so that the cyclodextrins, cyclodextrin derivatives or substances that form these compounds are added in an amount of 0.1 to 5 wt%, preferably 1 to 2 wt%, with respect to the amount of textiles to be rinsed. The substances can be added at any point in time in the washing or rinsing process, for example, at the start or during the process. In commercial washing processes the agent in accordance with the invention is preferably added at the beginning of the last rinse bath.

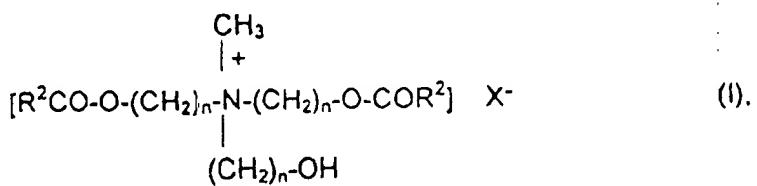
If the agent in accordance with the invention is in liquid form, it preferably contains water as primary solvent, which can be contained in amounts between 40 and 90 wt%, preferably between 60 and 90 wt%.

As a rule, the pH of a liquid agent in accordance with the invention lies between 1 and 13, in particular between 1 and 7.5 with laundry post-treatment agents in accordance with the invention, preferably above 4.5 and especially preferably between 5.5 and 6.5. Under conditions of use the pH of agents in accordance with the invention approximately corresponds to this. If an agent in accordance with the invention is used as detergent, the pH as a rule will be in the

alkaline range, while when it is used as a laundry post-treatment agent a pH in the acid to neutral range is preferred. To establish a low pH, the acids that are usual in this field, such as phosphoric acid, hydrochloric acid, glycolic acid, citric acid, lactic acid and formic acid and mixtures of these, can be used. The amount of acids is usually set by the desired pH value of the agent or the application purpose.

As softening agents the agents in accordance with the invention can contain the usual substances that are known from this field, preferably in amounts between 0.5 and 15 wt%, [most] preferably between 1.5 and 5.5 wt%, with respect to the prepared agent.

Preferred are softening agents with the formula I



in which R^2CO stands for an aliphatic acyl residue with 12 to 22 carbon atoms and 0, 1, 2 or 3 double bonds, n stands for 2 or 3 and X stands for halide, methosulfate or methophosphate.

Typical examples of the acyl residue R^2CO derive from fatty acids like caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, petroselic acid, linoleic acid, linolenic acid, arachic acid, gadoleic acid, behenic acid and erusic acid, as well as their industrial mixtures. Preferred are ester quats based on stearic or hardened tallow fatty acid in the form of their chlorides or methosulfates.

In addition, the agents in accordance with the invention can contain still other conventional components and additives that are usually contained in washing or laundry post-treatment agents. Examples of these are builders, enzymes, inorganic salts like carbonates, hydrogen carbonates, sulfates and silicates, softening agents, dyes and fragrances, pearlescent agents, solvents such as ethanol propylene glycol or glycol ether, soil repellents, thickeners and/or optical brighteners.

The solid components mentioned above such as builders and inorganic salts are contained in particular in an agent in accordance with the invention when it is in particulate form.

If the agent in accordance with the invention is in paste form, as a rule it contains builders and inorganic salts as well as thickeners, besides water and solvents.

Particularly suitable as builders are the known zeolites, crystalline layer silicates and salts of polycarboxylic acids such as citrates and/or (co)polymeric polycarboxylates.

Possibilities as enzymes are ones from the class of proteases, lipases or lipolytic enzymes, amylases, cellulases or their mixtures. Particularly well suited are enzymatic active agents obtained from bacterial strains or fungi such as *Bacillus subtilis*, *Bacillus licheniformis*, *Streptomyces griseos* and *Humicola insolens*. Proteases of subtilisin type and in particular proteases that are obtained from *Bacillus lenthutus* are preferably used.

The agents in accordance with the invention can be added directly to the rinse liquid during the wash cycle or in a rinse operation after washing, preferably in the last rinse operation.

Another object of this invention is the use of cyclodextrin, cyclodextrin derivatives or substances that form cyclodextrin or cyclodextrin derivatives in the rinse liquid or mixtures of these to improve the solubility of nonionic surfactants, in particular to avoid the deposition of nonionic surfactants on the textile being treated with a detergent containing these substances. The substances described above are added during the wash cycle as an additive or in a rinse operation after washing. They are appropriate both in washing or laundry post-treatment agents for use in the home as well as for commercial laundries.

Still another object of this invention is a method for treating textiles, which is characterized by the fact that during the wash cycle or in a rinsing step after washing cyclodextrin, cyclodextrin derivatives or substances that form cyclodextrin or cyclodextrin derivatives or mixtures of these are added to the wash liquid or rinse liquid during the wash cycle or in a rinse step after washing.

Examples

A commercial washing machine (E-Lux, FLE 120 MP) was loaded with 8.5 kg bulk laundry. Cotton beaver (Hohenstein test fabric) was used as test fabric. The laundry was washed for 10 min at 70°C with Pur Compactat® (commercial product of the applicant) as detergent in a concentration of 10 g detergent per kilogram of laundry. The bath ratio (weight ratio of laundry to water) was 1:5. Then the laundry was rinsed two times with cold soft water and one time with cold hard water (laundry:water = 1:7), 3 min each time. Cyclodextrin was added to the last rinse operation in a concentration of 3 g/L.

The residual surfactant content remaining on the laundry was 134 ppm.

In a comparison test cyclodextrin was not added to the rinse operation. The residual surfactant content was 209 ppm.

The reduction of the residual surfactant content in the example in accordance with the invention was 36% compared to the comparison test. It becomes clear from the examples that the addition of cyclodextrin to the last rinse operation brings about a clear reduction of the residual surfactant on the textiles.

Claims

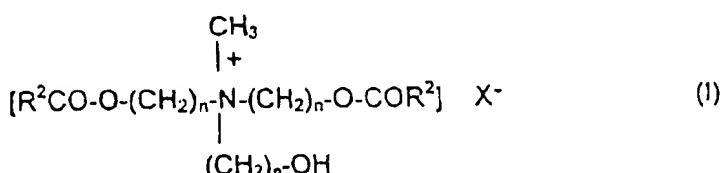
1. A powder, paste or liquid washing or laundry post-treatment agent, which is characterized by the fact that cyclodextrin, cyclodextrin derivatives, substances that form cyclodextrin or cyclodextrin derivatives in the rinse liquid or mixtures of these are contained as additive.

2. An agent as in Claim 1, which is characterized by the fact that α -, β - and/or γ -cyclodextrins or cyclodextrin derivatives are used.

3. An agent as in Claim 1 or 2, which is characterized by the fact that cyclodextrin, cyclodextrin derivatives or substances that form cyclodextrin or cyclodextrin derivatives in the rinse liquid or mixtures of these are added in an amount of 0.1 to 5 wt% with respect to the weight of the textiles to be cleaned or rinsed.

4. An agent as one of Claims 1 to 3, which is characterized by the fact that it has a pH value between 1 and 13.

5. An agent as in one of Claims 1 to 4, which is characterized by the fact that quaternary ammonium compounds of formula I



in which $R^2\text{CO}$ stands for an aliphatic acyl residue with 12 to 22 carbon atoms and 0, 1, 2 or 3 double bonds, n stands for 2 or 3 and X stands for halide, methosulfate or methophosphate is contained as softening agent.

6. An agent as in one of Claims 1 to 5, which is characterized by the fact that the compounds of formula I are contained in an amount of 0.5 wt% to 15 wt%, preferably 1.5 wt% to 5.5 wt%.

7. An agent as in one of Claims 1 to 5, which is characterized by the fact that the agent contains other components that are conventional in washing or laundry post-treatment agents such as builders, enzymes, inorganic salts, acids, pearlescence agents, solvents, dyes and fragrances and/or optical brighteners.

8. The use of the agent as in one of Claims 1 to 7 as a laundry post-treatment agent in the home and/or in commercial laundries.

9. The use of cyclodextrin, cyclodextrin derivatives or substances that form cyclodextrin or cyclodextrin derivatives in the rinse liquid or mixtures of these to improve the solubility of

nonionic surfactants, in particular to avoid the deposition of nonionic surfactants on the textile treatment with a detergent containing these substances.

10. A method for treating textiles, which is characterized by the fact that cyclodextrin, cyclodextrin derivatives or substances that form cyclodextrin or cyclodextrin derivatives in the rinse liquid or mixtures of these are added to the rinse liquid during the wash cycle or in a rinsing step after washing.

INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/EP 97/05092

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/22 C11D1/62

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 8833 Derwent Publications Ltd., London, GB; Class D25, AN 88-231738 XP002055460 & JP 63 165 498 A (LION CORP) , 8 July 1988 see abstract	1-4,7,8
A	---	5
X	DATABASE WPI Section Ch, Week 9616 Derwent Publications Ltd., London, GB; Class D25, AN 96-157617 XP002055461 & JP 08 041 780 A (NIKKA KAGAKU KK) , 13 February 1996 see abstract	1-4,7,8

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

12 February 1998

02/03/1998

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/05092

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9011 Derwent Publications Ltd., London, GB; Class A97, AN 90-080396 XP002055462 & JP 02 034 693 A (KAO CORP) , 5 February 1990 see abstract ---	1-4, 7
X	EP 0 301 847 A (MICROGENICS CORP) 1 February 1989 see page 3, line 3 - page 4, line 32; claims 1-6,10 ---	9
A	WO 94 06899 A (HENKEL KGAA) 31 March 1994 cited in the application see claim 1 ---	1.5
A	DATABASE WPI Section Ch, Week 9303 Derwent Publications Ltd., London, GB; Class A11, AN 93-023457 XP002055463 & JP 04 351 603 A (TOPPAN PRINTING CO LTD) , 7 December 1992 see abstract -----	1.9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/05092

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0301847 A	01-02-89	JP 1126400 A	18-05-89
WO 9406899 A	31-03-94	EP 0659207 A JP 8501579 T US 5627144 A	28-06-95 20-02-96 06-05-97